Equation of State and Thermodynamic Properties of Dilute Supercritical Aqueous n-Hexane Solutions

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The use of dilute supercritical mixtures of hydrocarbons in water at high temperatures and high pressures is of considerable interest in energy resource production (hydrothermal synthesis, formation of petroleum, reservoir fluids, enhanced oil recovery via steam and tertiary methods), environmental protection (removal of hydrocarbons from waste water, the fate of hydrocarbons in geological fluids), new separation techniques, and biological degradation without char formation. However, a realization of the potential of supercritical fluid solubility will prove to be impossible without a better knowledge and models of the thermodynamic properties of fluid mixtures near the solvent (pure water) critical point.

In this work, we have applied the parametric crossover model incorporated in the CREOS97 computational model to the description of the phase behavior and thermodynamic properties of critical dilute aqueous hexane mixtures, which according to the Konynenberg-Scott specification, corresponds to a Type III mixture. All system-dependent parameters of this model are expressed as functions of the excess critical compressibility factor of the mixture. Therefore, if the critical locus of the mixture is known, all other thermodynamic properties can be predicted. In order to identify $\rho_c(x)$ critical locus at $x \to 0$, we have measured the *PVTx* properties of dilute water + n-hexane mixtures in the vicinity of the critical point of pure water. These *PVTx* data together with $T_c(x)$ and $P_c(x)$ critical locus data reported earlier by de Loos have been used to develop a crossover equation of state for water + n-hexane mixtures in the wide region around the critical point of pure water. In the binary water + n-hexane solutions, the CREOS yields an adequate description of all available experimental data in the region bounded by $0.35\rho_c(x) \le \rho \le 1.65\rho_c(x)$ and $0.98T_c(x) \le T \le 1.15T_c(x)$ at $x \le 0.07$ mole fraction of n-hexane. A possibility of the extrapolation of the CREOS at lower temperatures, $0.93T_c \le T \le T_c$, and higher densities and concentrations is also discussed.